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Modular assembly of conformationally dynamic dinaphthocycloocta-1,5-dienes

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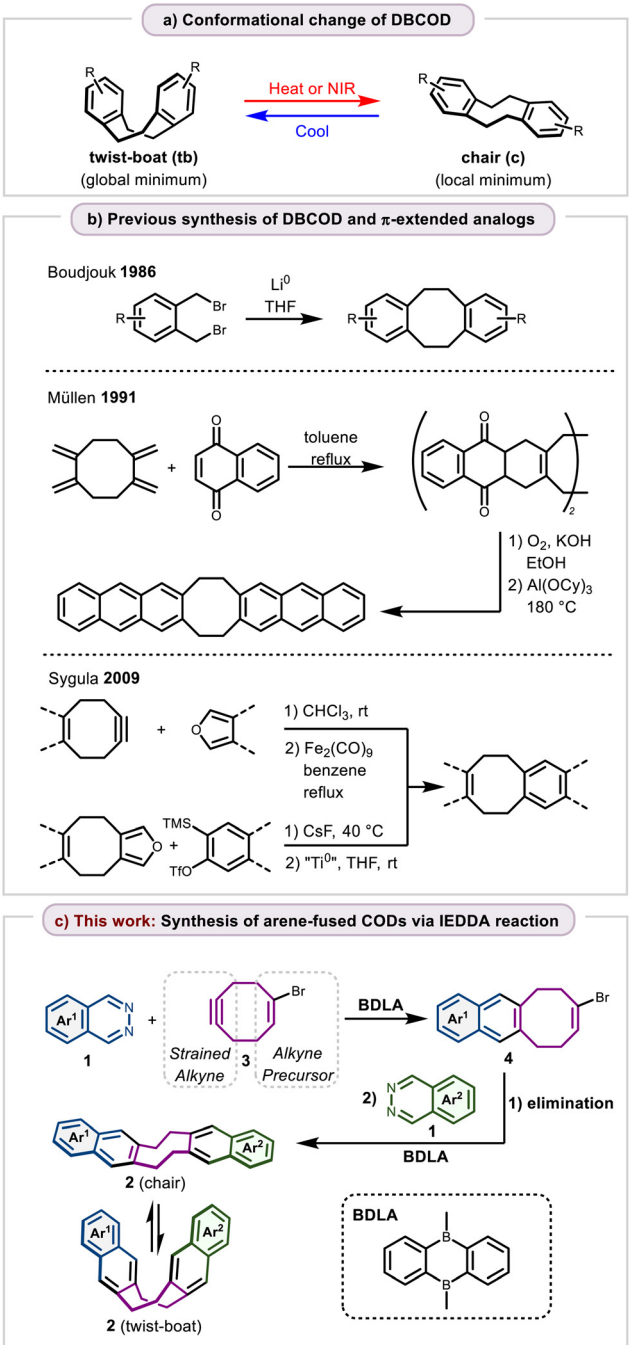
The integration of cyclooctene-derived motifs into larger molecular frameworks has emerged as a promising strategy to construct switchable molecules and materials that rely on conformational changes of the central eight-membered ring. In this work, we developed a facile synthetic route to access dinaphthocycloocta-1,5-dienes (DNCODs) relying on Lewis acid-catalyzed inverse electron-demand Diels–Alder (IEDDA) reactions of phthalazines and cyclooct-1-en-5-yne derivatives. By employing two sequential IEDDA reactions, the modular annulation of different naphthalene units to the cyclooctadiene core was achieved. While the resulting DNCODs were found to adopt a chair conformation in the crystalline state, variable temperature (VT) NMR spectroscopy revealed a dynamic equilibrium in solution, with the twist-boat conformer being favoured. These findings offer new opportunities for engineering switchable cyclooctene-based structures and integrating them into functional materials.

Introduction

Eight-membered carbo- and heterocycles fused to aromatic ring systems have emerged as versatile scaffolds in the construction of functional molecules and materials. The ability of eight-membered rings, especially cycloocta-1,5-dienes (CODs) and cyclooctatetraenes (COTs), to bring flexibility into larger, otherwise rigid polycyclic ring structures has led to their application in organic photonics and electronics,[1–4] molecular sensors,[5] and supramolecular assemblies.[6,7] In this regard, a new class of materials has been developed over the last decade based on conformational changes of dibenzocycloocta-1,5-diene (DBCOD), which consists of a flexible eight-membered ring fused to two rigid aromatic rings on opposite sites. Lu and coworkers were the first to describe a DBCOD-containing polymer that exhibited an unusual and completely reversible thermal contraction triggered by NIR stimulation.[8] They further showed that this mechanical response arises from the thermally induced conformational change of DBCOD from the twist-boat (global minimum) to the chair (local minimum) conformer (Scheme 1a).[9] This intriguing conformational effect led to extensive research not only on DBCOD in material applications,[10–22] but also aiming at better understanding and fine-tuning this new type of molecular switch as well as its heterocyclic analogues.[23–26] In a comprehensive study, Lu and coworkers showed that the twist-boat conformer can be stabilized by substituents capable of forming intramolecular hydrogen bonds while the chair conformer is stabilized by repulsive substituent interactions.[23] The DBCOD derivatives used in this study were synthesized by dimerizing substituted α,α′-dibromo-*o*-xylene in the presence of lithium metal as previously described by Boudjouk and co-workers.[27] However, while this method yields symmetric dimerization products, DBCOD derivatives having differently substituted aromatic rings on opposite sides have rarely been prepared or investigated. Similarly, only a few methods for the synthesis of π-extended DBCOD analogues have been reported,[7,28] most of which require multiple-step preparation and do not offer a broad substrate scope (Scheme 1b). Furthermore, reported solubility issues prevented the investigation of the conformational behaviour of these compounds in solution.[7]

In light of these limitations, we reasoned that a modular synthetic approach to arene-fused CODs would be highly desirable to further enable systematic investigations and application of this class of molecular materials. We recently reported a method for the synthesis of arene-annulated cyclooctenes *via* inverse electron-demand Diels–Alder (IEDDA) reaction of phthalazines (**1**) and cyclooctynes catalyzed by a bidentate Lewis acid (**BDLA**).[29] The boron-based catalyst functions by lowering the LUMO energy of the diazine through complexation and thus facilitates the cycloaddition step.[30] Herein, we report the expansion of this strategy to the syn-

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Scheme 1 Conformational behaviour and synthesis of arene-annulated CODs.

thesis of naphthalene-fused CODs **2** by employing previously described (*E*)-1-bromocyclooct-1-en-5-yne (**3**) (Scheme 1c).[31] This dienophile contains a strained alkyne on one side and a vinyl bromide as a latent alkyne precursor on the opposite site,[7,32] which enabled the modular synthesis of dinaphtho-CODs (DNCODs) **2** by two sequential IEDDA reactions. Variable temperature (VT) NMR studies in combination with X-ray crystallography gave valuable insights into the conformational behaviour of these compounds.

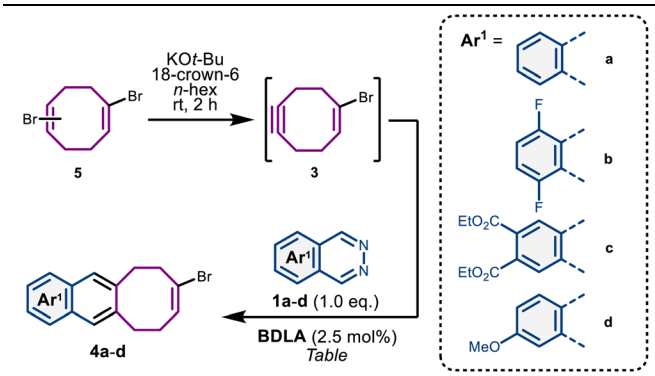
Results and discussion

Synthesis

To realize the envisaged synthetic strategy, we commenced our investigation with the IEDDA reaction of different phthalazines **1a–d** and alkyne **3** (Table 1), which can be easily prepared from cycloocta-1,5-diene over three steps. As the strained alkyne **3** is reported to be highly reactive and unstable,[31] we decided to use it in excess as a crude extract that has to be deoxygenated prior to the addition of the oxygen-sensitive **BDLA** catalyst. By treating this extract with a mixture of reactive, electron-poor difluorophthalazine **1b** and the catalyst, we were able to isolate the desired substituted naphthalene **4b** in 40% yield (Table 1, entry 1). With a larger excess of alkyne, the yield was improved to 60%. To make the reaction suitable for higher temperatures, the solvent was exchanged for 1,4-dioxane which resulted in a further increase in yield to 72%. Similarly, phthalazine **1c** carrying two ester groups underwent the IEDDA smoothly under the same conditions and furnished the substituted naphthalene **4c** in 78% yield. For less reactive unsubstituted phthalazine (**1a**) and methoxyphthalazine **1d**, yields in the same range were achieved by using a larger excess of alkyne and a slightly higher temperature of 100 °C (Table 1, entries 5 and 6).

With optimized conditions for the first IEDDA reaction of electron-poor, -neutral and -rich phthalazines in hand, we proceeded by subjecting the obtained vinyl bromides **4a–d** to the elimination reaction with KO*t*-Bu and catalytic amounts of 18-crown-6 ether (Scheme 2). Contrary to literature reports,[32]

Table 1 Reaction conditions of the IEDDA reaction of (*E*)-1-bromocyclooct-1-en-5-yne (**3**) with different phthalazines



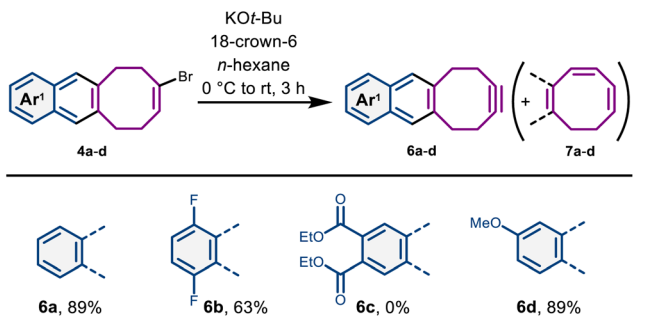
Entry	Ar^1	**5** (eq.)	Solvent	*T* (°C)	*t* (h)	Yield (%)
1[a]	**b**	1.5	EA/*n*-hex	Reflux	24	40
2[a]	**b**	2.5	EA/*n*-hex	Reflux	24	60
3[b]	**b**	2.5	1,4-Dioxane	80	24	72
4[b]	**c**	2.5	1,4-Dioxane	80	24	78
5[b]	**a**	4.0	1,4-Dioxane	100	48	72
6[b]	**d**	6.0	1,4-Dioxane	100	72	68[c]

[a] Crude extracts containing alkyne **3** were deoxygenated by bubbling nitrogen through the solution for 1 h. [b] Crude extracts containing alkyne **3** were concentrated *in vacuo*, re-dissolved in 1,4-dioxane and degassed by three freeze–pump–thaw cycles. [c] A 1 : 1 mixture of regioisomers was obtained (EA = ethyl acetate, *n*-hex = *n*-hexane).

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performing the reaction at elevated temperature (60 °C) did not yield the desired strained alkynes **6** in our case but rather resulted in the exclusive formation of dienes **7**. Temperatures below 0 °C led to an incomplete conversion with the diene formation still not completely suppressed. Optimal conditions with less than 10% diene formation and complete conversion were found by performing the addition at 0 °C and subsequent warming to room temperature. In that way, the strained alkynes **6a** and **6d** were obtained in 89% yield after filtration over silica. Alkyne **6b** bearing an electron-deficient aromatic part had to be purified *via* column chromatography, which resulted in a diminished yield of 63% together with 9% of diene **7b**. In the case of diethyl naphthalenedicarboxylate **3c**, treatment with KO*t*-Bu furnished a mixture of different transesterification products rather than the desired alkyne **6c**.

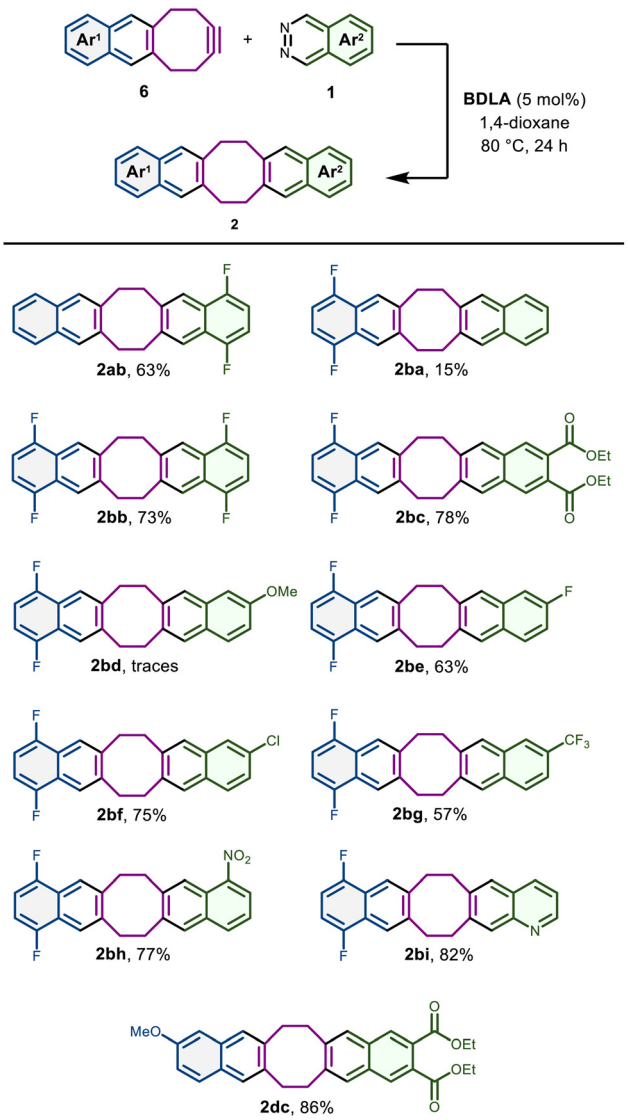
With three strained alkynes **6a,b** and **d** in hand, we set out to explore the scope of the second IEDDA reaction. Differently substituted phthalazines and pyridazino-aromatics were reacted with alkyne **6b** in the presence of the **BDLA** catalyst adapting the previously described conditions for analogous reactions with cyclooctyne (Scheme 3).[29] Good to excellent yields were achieved for the second IEDDA reaction with electron-deficient mono- and dihalogenated (**1b,e,f**) as well as CF_3- (**1g**), nitro- (**1h**) and ester-substituted (**1c**) phthtalazines. Similarly, pyridopyridazine **1i** furnished the desired quinoline **2bi** in a very good yield of 82%. Unfortunately, electron-neutral, unsubstituted phthalazine (**1a**) gave the desired DNCOD **2ba** only in 15% yield, alongside unreacted phthalazine and decomposition products of alkyne **6b**. Nevertheless, we were able to synthesize dinaphthalene **2ba** (= **2ab**) in a very good yield by reacting alkyne **6a** with difluorophthalazine **1b**. In that way, the yield for the synthesis of the desired DNCOD was improved from 10% (**2ba**) to 29% (**2ab**) over three steps simply by switching the order of phthalazines in the reaction sequence. Accordingly, only traces of product **2bd** could be isolated from the reaction of alkyne **6b** and electron-rich methoxyphthalazine **1d**. Methoxy-substituted dinaphthalene **2dc** was obtained in a very good yield by utilizing alkyne **6d**, though. Although this method is not suitable for the synthesis of DNCODs with two electron-rich aromatic parts, it enables many other possible combinations, provided that at least one aromatic unit is electron-deficient. In addition to the electronic nature of the employed phthalazine, the solubility of the resulting dinaphthalenes had a significant influence on the yields. With the exception of **2bc**, **2bi** and **2dc**, all other DNCODs showed only very limited solubility in common organic solvents. Thus, recrystallization was sometimes preferred over chromatography for purification, which in turn led to reduced yields.



Scheme 2 Synthesis of naphthalene-fused cyclooct-1-en-5-ynes **6** *via* elimination. Reaction conditions: vinyl bromide **4a–d** (0.6–0.7 mmol, 1 equiv.), KO*t*-Bu (1.6–1.7 mmol, 2.5 equiv.) and 18-crown-6 (0.16–0.17 mol, 0.25 equiv.) in anhydrous *n*-hexane (50 mL).

Conformational study

With a modular route for the synthesis of diversely substituted DNCODs established, we focused on a detailed examination of the conformational preferences of the target compounds.



Scheme 3 Scope of phthalazines in the second IEDDA reaction. Reaction conditions: alkyne **6a,b,d** (0.1 mmol, 1 equiv.), phthalazine **1a–i** (0.1 mmol, 1 equiv.) and **BDLA** (5 μmol, 5 mol%) in 1,4-dioxane (2 mL).

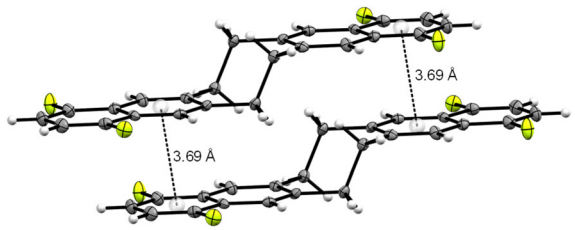


Fig. 1 Solid-state structure of DNCOD **2bb** (CCDC: 2433662). Thermal ellipsoids are shown at 50% probability.

DBCODs lacking intramolecular hydrogen bonding have been reported to preferentially crystallize in the chair conformation.[23,33] In line with these findings, we observed that our DNCODs adopt the same conformation in the solid state due to energetically favourable π–π interactions, as confirmed by X-ray crystallographic analysis of tetrafluoro derivative **2bb** (Fig. 1). However, solutions of (substituted) DBCODs have been reported to contain mixtures of chair and twist-boat conformers in varying ratios, depending on the temperature and substitution pattern.[23] Additionally, earlier reports identified a twist form as a third local minimum conformation. This twist conformer, although reported to be too high in energy to be present in solution in significant amounts, is thought to represent a pivotal intermediate in several interconversion pathways.[34]

Given these findings, we aimed to investigate the in-solution behaviour of our DNCODs by VT NMR spectroscopic analysis. As model substrates, we chose naphtho-CODs **2bc** and **2dc**, as they both feature two electron-withdrawing ester substituents on one naphthalene unit and differ significantly in the electronic nature of the second aromatic ring system. Additionally, both compounds exhibited good solubility in common organic solvents, even at low temperatures.

At 20 °C, the ^{1}H NMR spectra of both compounds displayed only merged signals from the twist-boat and the chair conformers (Fig. 2). Upon cooling, all signals further broadened until the coalescence temperature T_c was reach between 0 °C and −10 °C. Below −10 °C, the interconversion rate of both conformers slowed down sufficiently, allowing the individual signals of the twist-boat and chair conformers to be detected. While the methylene protons of the eight-membered ring in the chair conformer showed two distinct signals belonging to the axial and equatorial protons, only one, broadened peak was observed for the twist-boat due to rapid boat inversion even at −45 °C.[35] Further cooling to −60 °C slowed down this inversion, causing the broad singlet to split up into two separate

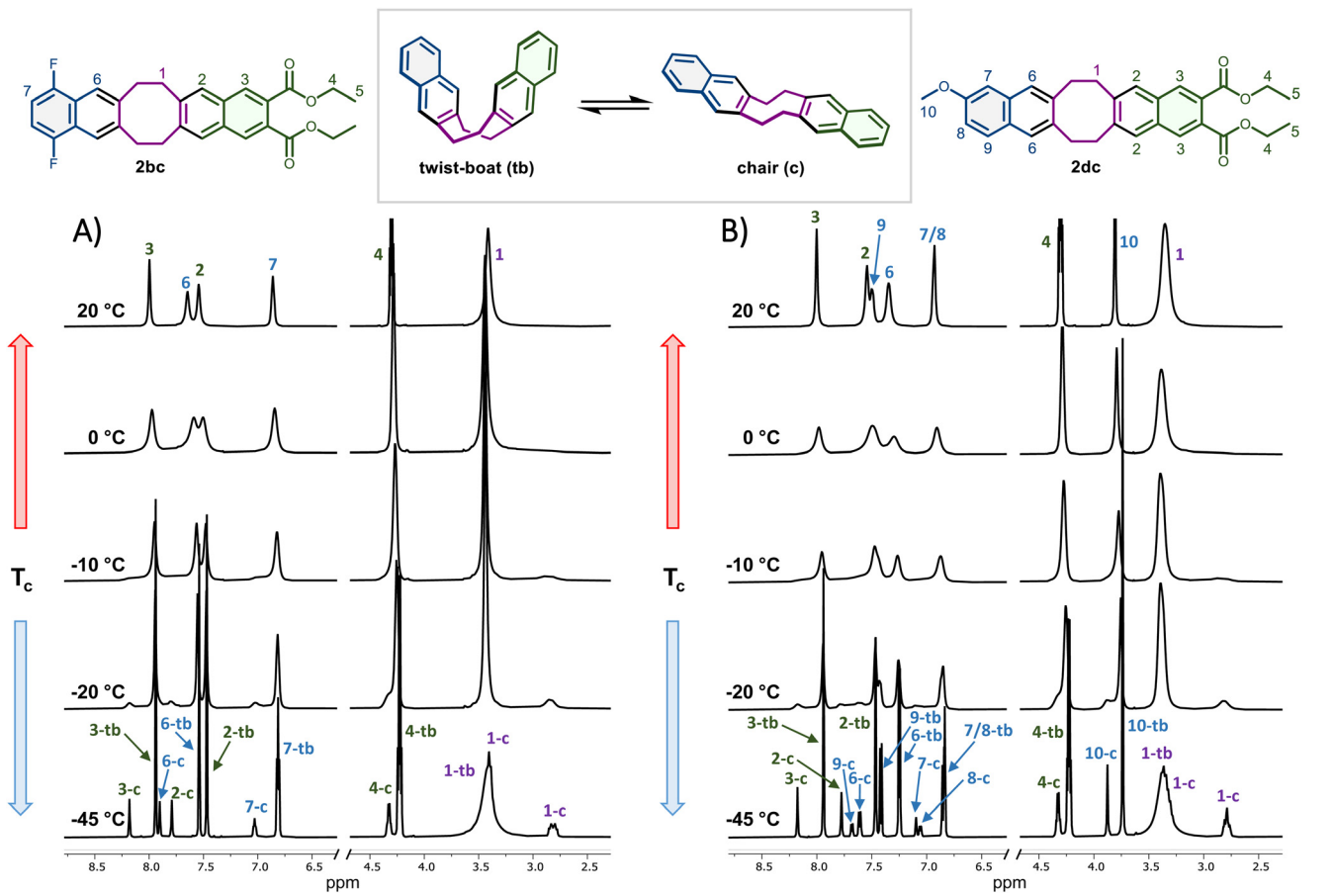


Fig. 2 Variable temperature ^{1}H NMR (600 MHz) spectra with peak assignment of DNCODs **2bc** (A) and **2dc** (B) in CD_2Cl_2 (c = chair, tb = twist-boat).

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signals (see Fig. S5). In the aromatic region, proton resonances of the chair conformer appeared at higher frequencies compared to the twist-boat, due to reduced shielding in the former.[36] Across the entire temperature range, the twist-boat conformer was found to be the dominant form. This experimental observation is supported by our computational analysis (see section 3 of the SI), which also identified the twist-boat as the most stable conformer, followed by the chair. The twist form, however, was found to be too high in energy to be present in detectable amounts.

The VT NMR data enabled the determination of the thermodynamic and kinetic parameters of the twist-boat/chair equilibrium. The spectra acquired below T_c were used to calculate the Gibbs free energy difference $\Delta G°$ between the twist-boat and chair forms of DNCODs **2bc** and **2dc** based on the relative populations of both conformers obtained by integration (see section 2.2.2 of the SI).

For both derivatives, the twist-boat conformer was found to be thermodynamically favoured by 2.8 kJ mol^{-1} at 25 °C, corresponding well to the observed twist-boat-to-chair ratio of approximately 3 : 1 at this temperature. The equilibrium only shows a minor temperature dependence, with a temperature increase from −80 °C to 25 °C resulting in just a 10% increase in the chair population (see SI). These values indicate that DNCODs generally exhibit a stronger preference for the twist-boat conformation across a wider temperature range compared to related DBCOD derivatives. As both naphthalene units in one DNCOD are too far apart to show any non-covalent intramolecular interactions, even in the twist-boat form (see Fig. S12 and S13), no effect of the electronic nature of the aromatic rings was observed.

For the determination of the kinetic parameters of the equilibrium, rate constants of the interconversion were obtained *via* dynamic NMR lineshape analysis. Temperature-dependant signal broadening resulting from chemical exchange on the NMR timescale was analyzed by fitting the experimental line shapes to appropriate exchange models, yielding rate constants at different temperatures. Subsequent Eyring–Polanyi analysis gave access to the activation parameters, including enthalpies and entropies of activation, from which the Gibbs free energies of activation ($\Delta G^{\ddagger}$) were derived (see section 2.2.3 of the SI).

For DNCODs **2bc** and **2dc**, similar Gibbs free energies of activation of 53.5 kJ mol^{-1} and 55.5 kJ mol^{-1}, respectively, were obtained, with both derivatives showing negative entropies of activation for the conformational change. This barrier is about 10 kJ mol^{-1} higher than that reported for unsubstituted DBCOD and more comparable to values previously obtained for derivatives, where intramolecular hydrogen bonding stabilizes the twist-boat conformer.[23,34] However, as mentioned above, no such interactions, nor comparable ones, were identified for the DNCODs **2bc** and **2dc** through our computational analysis. This further underlines that naphthalene units fused to a COD core generally provide a greater stabilization of the twist-boat conformer in comparison to benzannulated analogues.

Conclusions

In summary, we developed a concise route for the synthesis of substituted DNCODs from readily available phthalazines, employing two sequential BDLA-catalyzed IEDDA reactions. The first IEDDA reaction furnished bromocyclooctanaphthalenes **4a–d** in good yields with electron-poor and electron-rich phthalazines under optimized conditions. Subsequent base-mediated elimination afforded comparatively stable cyclooctenynes **6a**, **6b** and **6d**, which were further converted into the desired DNCODs *via* a second IEDDA reaction. This sequence enabled the direct annulation of differently substituted naphthalenes to the COD core in a modular fashion. X-ray crystallographic analysis of dinaphthalene **2bb** revealed that these DNCODs adopt a chair conformation in the solid state. In solution, however, the twist-boat form was found to predominate independent of the electronic nature of the naphthalene units. Furthermore, the activation energy of the twist-boat/chair interconversion was found to be slightly higher compared to related DBCOD derivatives, as determined by DNMR spectroscopy. These results provide a basis to guide future developments in the design of switchable molecules relying on conformational interconversions of cyclooctene-derived scaffolds and foster their integration into functional materials.

Author contributions

M. G. and H. A. W. conceptualized the project. M. G. performed the organic synthesis and collected experimental data. C. M. L. performed the DFT calculations. All authors were involved in discussing the data and preparing the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5qo01621e**.

CCDC 2433662 (**2bb**) contains the supplementary crystallographic data for this paper.[37]

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